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(19) (CA) # CANADIAN PATENT

(54) CELL JACKET FOR METAL/AIR OR METAL/OXYGEN CELLS

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Granted to Hitachi Maxell Limited, Ibaraki-shi, Osaka, Japan

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No. OF CLAIMS 23

This invention relates to primary and secondary metal/air cells. More particularly, this invention is directed to metal/air cells comprising a consumable metal anode, an electrolyte, and an air depolarized cathode comprising a pressure deformable, hydrophobic member in contact with an electrocatalyst, the cell preferably having a cylindrical configuration.

In the copending application of Hong Po Louie, Serial No. 050,143 filed April 30, 1969, there is described an improved metal/air cell structure comprising a cathode composed of a hydrophobic polymer member having an electrocatalyst on its inner surface. The polymer member is positioned within a rigid jacket having perforations constituting air vents therein. In a typical embodiment, the cathode is of cylindrical tubular construction, and an anode of porous consumable metal, such as, for example, zinc, in the shape of a rod is positioned axially within the cathode. This anode may be retained in proper position by attachment to an end closure for the jacket, the closure being constructed and arranged to form a liquid-tight seal with the outer jacket. A suitable electrolyte fills the entire space between the anode and the cathode, except for a hydrophilic separator positioned in contact with the electrocatalyst of the cathode. The electrolyte may be "dry" for subsequent activation with water when the cell is to be placed in use, or the electrolyte may be in a liquid state, having the form of a thick paste or gel, so that the cell is ready for use without special activation. If a cylindrical cell configuration is selected, it is desirable to provide the cell with terminal plates at each end of the jacket, one of these terminal plates being electrically connected to the anode and the other terminal plate being electrically connected to the cathode.

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The metal/air cell operates to produce electrical energy in a known manner in that the electrocatalytic surface converts oxygen from the ambient air into hydroxyl ions, the air reaching the cathode through the perforations in the cell jacket. The ions travel through the electrolyte and are collected at the zinc anode, which undergoes conversion to zinc oxide. When an external circuit path is completed between the anode and the cathode of the cell, the electrons which are given up at the anode flow as an electrical current through this externally completed circuit path.

During operation of the cell, performance is degraded because of an internal increase in pressure on the cathode as the anode and the electrolyte undergo physical and chemical change. For example, it is noted that zinc oxide formed when zinc is the electrochemical compound, has 1/3 more volume than zinc. This internal pressure causes separation of the cathode layers including the electrocatalyst and the polymer membrane, and as well, disruption of the electrical connection between the cathode and its terminal plate.

Accordingly, it is an object of a principal aspect of the present invention to provide a metal/air cell, preferably of cylindrical configuration, in which cell degradation caused by internal pressure during operation is circumvented.

It is an object of a more specific aspect of the present invention to provide means for reducing the disruptive effect of the internal pressure on the cathode of a cylindrical metal/air cell during operation of the cell, preventing separation of the cathode layers and the destruction of the electrical connection between the cathode and a terminal plate for the cell.

According to broad aspects of this invention, a perforated restraining tube, formed of a plastic material, is provided about the cathode and in direct contact therewith. The

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perforations in this restraining member permit air to enter the cell via the vents in the rigid jacket and to reach the cathode, while the restraining member itself exerts sufficient radial pressure on the cathode, relative to the axis of the overall cell, to oppose the radially outwardly directed forces created by the internal pressure occurring during cell operation.

Thus, by one broad aspect of this invention, a metal/air or metal/oxygen cell is provided, comprising: a consumable metal anode; a pressure deformable cathode spaced apart from and encompassing, said anode, said cathode comprising a pressure deformable, gas permeable, hydrophobic membrane having, in intimate contact therewith, an inner face, relative to said anode, of electrocatalytic material; an electrolyte in the space separating the anode and the cathode; means sealing said anode, said cathode and said electrolyte to prevent the escape of electrolyte from said space while providing electrical access to said anode and said cathode; and ventilation means encasing said cathode to permit air or oxygen to come into contact therewith, said ventilation means including an electrically insulative plastic restraining member having apertures tightly encompassing said cathode to restrict outward movement of the cathode in response to internal pressure exerted thereon during operation of said cell.

By another aspect of this invention, a metal/air or metal/oxygen cell is provided, comprising: a metal electrode; a thin, pressure deformable, oxygen electrode concentrically surrounding said metal electrode and spaced apart therefrom; an electrolyte in the space between said cathode and said anode; and a restraining plastic member surrounding said cathode in tight contact therewith to resist the internal pressure exerted on said cathode as the cell ages, said restraining member having holes therein to permit ambient air to

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reach said cathode.

In a preferred embodiment of the invention the cathode restraining member is composed of a heat shrinkable or heat contracting material, i.e., a material which shrinks or contracts upon exposure to heat and remains in the contracted state after heat is removed, such as, for example, a tubing of polyvinyl chloride, irradiated polyethylene, modified nylon, polytrifluoroethylene, polydifluoroethylene, polyethylene-terephthalate, etc. As a consequence, heating of the cell before operation causes shrinkage of the heat contracting material, thereby increasing the inwardly directed forces on the cathode, and thereby tending to equalize the inwardly and outwardly directed pressures on the cathode.

In the accompanying drawings:

Figure 1 is a perspective view, partly broken away, of a metal/air cell according to the invention;

Figure 2 is a cross-sectional view of the metal/air

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cell of FIGURE 1; and

FIGURE 3 is an enlarged detailed view, in fragmentary cross-section, of the cathode of the metal/air cell in FIGURES 1 and 2.

With reference now to the drawings, the overall cell 10 is, in the preferred embodiment, of cylindrical construction, and includes a tubular cathode (or oxygen electrode) 11. Preferably, the cathode 11 comprises a gas pervious, hydrophobic polymer membrane or film 12, of polytetrafluoroethylene for example. The polymer membrane is coated on its internal surface, relative to the axis of the cell, with an electrocatalyst layer 13 composed for example of silver particles in a polytetrafluoroethylene particle binder. A metal support screen 14 may be embedded in the electrocatalyst layer 13 to provide support for the overall cathode tube and to provide a convenient electrical connecting surface to the cathode terminal plate as will be described presently. Preferably, the metal support screen 14 is a nickel mesh.

In the preferred embodiment, the anode composed of amalgamated zinc powder and a suitable electrolyte, such as for example potassium hydroxide, in the form of a gel or paste completely fill gap 16 except for current collector 15 and hydrophilic separator 17. The separator, such as for example a layer of glassine paper is positioned in intimate contact with the electrocatalytic surface of the cathode.

Insulative disks 18 composed of plastic, rubber, or the like are provided at either end of the cell adjacent the

electrolyte to seal the electrolyte within the cell. Metal terminal plates 19 and 20 for the cathode and the anode, respectively, are provided at the ends of the cell and are electrically connected to the respective electrodes. Conventional gaskets 21 and 22 are utilized at each end of the cell to provide an appropriate insulative seal between the cell jacket 23 and the electrode terminal plates 19 and 20. The cell jacket 23 is composed of rigid sheet material, preferably metal although a hard plastic material may alternatively be used, formed in a cylindrical tubular structure. The jacket is perforated throughout with air vents 24 to permit ambient air externally of the cell to enter the cell and reach the cathode.

During operation of the battery to produce electrical energy, the anode and the electrolyte undergo chemical change, with zinc oxide forming at the anode and potassium carbonate forming in the electrolyte, for example. As noted hereinabove, the volume of zinc oxide is approximately one-third more than zinc. Accordingly, the chemical change is accompanied by a physical change in the cell, manifested by an expansion of the body of the cell primarily in a radially outward direction relative to the cell axis or center. As a result of the expansion of the cell body, an ever-increasing internal pressure is exerted on the cathode member causing deformation of that member, particularly along its midsection, and setting up stresses at its point of contact with the seals and the terminal plate. Such effects can seriously shorten the life of the cell by causing the separation of the cathode layers 12, 13, and 14 one from the other, as well as the possible rupture of the electrocatalyst layer 13 and the polymer membrane 12, and the disruption

of the electrical connection between metal screen 14 and terminal plate 19.

The present invention provides a substantial reduction in the likelihood that such separation, rupture and disruption will occur, and hence an increase in the useful life of the battery, by means of the use of a restraining member 25 about and in immediate contact with the external surface of the cathode. For a cell of cylindrical shape, as is the preferred embodiment here, restraining member 25 is a thin-walled tube and is composed of any suitable electrically insulative material capable of resisting the outward pressure exerted on the cathode 11 as the cell body undergoes expansion. Suitable materials include vinyl resins and rubber. If desired, the restraining member may sufficiently tightly encompass the cathode to exert an inwardly directed pressure tending to equalize the outward pressure caused by cell expansion.

Like cell jacket 23, restraining member 25 is also perforated throughout with air vents 26 to permit ambient air to reach the cathode.

The anode material utilized in the cell may be any conventional electro-conductor employed in a metal/air or metal/oxygen cell. It is only essential that the material selected be chemically reactive with a compatible electrolyte and be more electro-positive than oxygen. Suitable materials include lead, zinc, iron, cadmium, aluminum, and magnesium. From the standpoint of cost, capacity, and convenience, porous zinc is the preferred anode material, as noted hereinabove. Although a porous anode is preferred, a solid metal sheet or rod is operable.

Suitable electrolyte materials include alkali metal hydroxides, mixtures of alkali metal hydroxides, acid or basic anhydrides or hydrolyzable salts, e.g., alkali metal oxides and salts of weak acids, ammonium salts of strong acids, oxides of non-metals such as phosphorus and the like. However, an alkali metal hydroxide, such as for example potassium hydroxide, is preferred as was noted earlier. Preferably, too, the electrolyte is in the form of an aqueous gel or paste.

The cathode will comprise an electrically conductive, porous, pressure deformable substrate in contact with a catalytic metal or a catalytic metal in admixture with a hydrophobic polymer such as for example a polyhaloalkylene, a polyester, a polyalkylene or the like. As the term is employed herein, "pressure deformable" embraces materials which are highly flexible and rupturable. As stated earlier, the cathode substrate preferably includes a gas pervious, hydrophobic polymer membrane or film to which the electrocatalytic layer is adhered as an inner face. This catalytic layer can comprise a metal, metal oxide, or metal alloy of Groups I-B, II-B, IV, V, VI, VII and VIII of the Mendelyeev's Periodic Table, mixed with a binder composed of particles of one of the aforementioned hydrophobic polymers. The electrically conductive porous support may be a screen composed of any metal resistant to corrosive attack by the electrolyte. Suitable screen materials include the metals of the second and third triads of Group VIII, nickel, cobalt, silver, gold, various ferrous alloys, titanium, hafnium, zirconium, chromium, alloys of these and the like. In operation of a cell using such cathodes, it is essential that the polymer substrate be in

contact with the electrocatalyst, and if used, with the support screen. If delamination occurs, the cell will be inoperative. The invention prevents such delamination as noted hereinbefore.

The seals, gaskets, and closures preferably comprise lightweight electrically non-conductive materials such as for example synthetic resins, namely, a polyalkylene or the like.

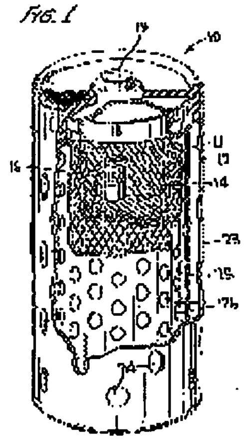

Fig. 1

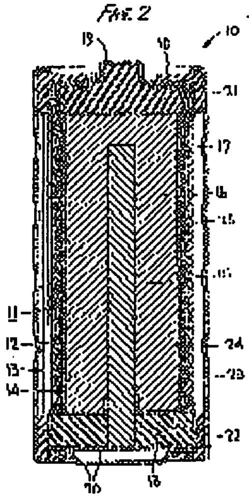

Fig. 2

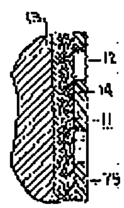

Fig. 3

INVENTORS

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